

Superconductivity and Cobalt Oxidation State in $\text{Na}_x\text{CoO}_2 \cdot 4x\text{H}_2\text{O}$ ($x \approx 1/3$)

Scientific Achievement

We have extensively investigated how changing the average cobalt oxidation state (n) affects superconductivity (T_c) in sodium cobaltate hydrate, $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$. Its structure contains two-dimensional CoO_2 hexagonal planes formed from face-sharing CoO_6 octahedra that are separated by layers of distorted $\text{Na}(\text{H}_2\text{O})_4$ tetrahedra. The water molecules in the $\text{Na}_x(\text{H}_2\text{O})_{4x}$ layers are oriented as to form an extensive hydrogen bonding network throughout the lattice. Using neutron powder diffraction, we show that metastable $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ slowly forms oxygen vacancies, which directly affects the Co oxidation state and T_c of the material. Using a single $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ sample, we mapped its superconducting phase diagram. T_c (~2.2 K) was first observed when $n \approx +3.6$ and reached a maximum value (4.5 K) when $n \approx +3.5$. Superconductivity rapidly disappeared as cobalt reduction continued. We speculate that destruction of superconductivity in this metastable material is due to charge ordering when the cobalt oxidation state is +3.5.

Thermal expansion and compressibility of $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ were monitored using neutron powder diffraction over the temperature range of 10-295 K and the pressure range of 0-0.6 GPa. While anisotropic thermal expansion occurred ($\Delta c/c > \Delta a/a$) as expected with increasing temperature, the effects of increasing pressure were surprising. The thickness of the CoO_2 layers increased as a function of increasing pressure. Two parameters control this layer thickness – the Co–O bond length, and the O–Co–O angle. This unusual increase in layer thickness is attributed to pressure-induced strengthening of the hydrogen bonding between the CoO_2 layers and the intercalated D_2O molecules. The strengthened H-bonds require a charge redistribution that weakens the Co–O bonds, thus decreasing the average cobalt oxidation state in this material.

Significance

This project is part of an ongoing program on layered superconductors. We show how neutron powder diffraction can be combined with other techniques to probe the variables (defect concentrations, charge states, etc.) that affect the electronic structure and physical properties of a material. Additionally, these results have broader implications on how superconductivity in $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ should be viewed. There are more than two variables (Na and D_2O content) that affect the superconducting properties of this material. The cobalt oxidation state is an important variable that can be decreased by oxygen vacancy formation under ambient conditions or pressure-induced charge redistribution. Previous interpretation of superconducting phase diagrams and pressure effects on T_c should be reconsidered based on these new findings. This highlight summarizes the results found in three different publications: J. D. Jorgensen *et al.*, *Phys. Rev. B* **68**, 214517 (2003); P. W. Barnes *et al.*, *Phys. Rev. B* **72**, 054428 (2005); and J. D. Jorgensen *et al.*, *Phys. Rev. B* **72**, 224515 (2005).

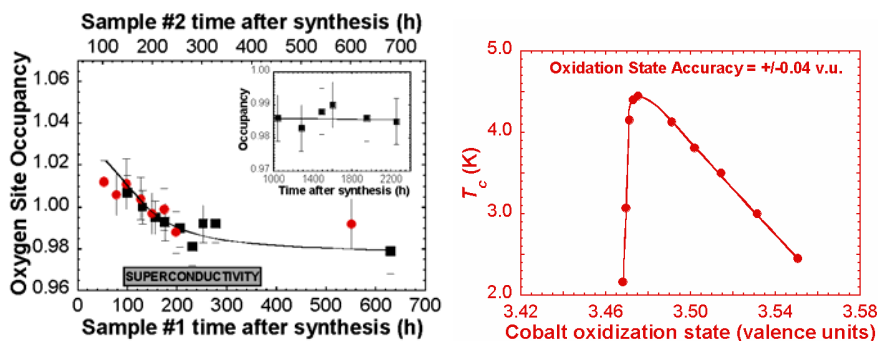
Performers

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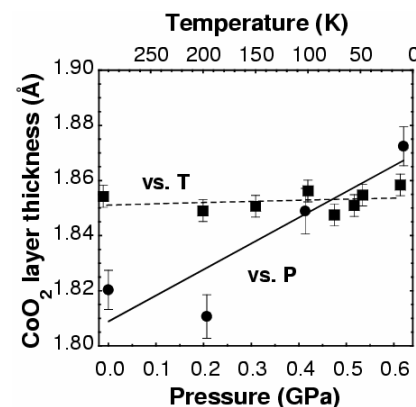
- Changes in $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ electronic structure affect its superconducting (SC) properties
- Use neutron powder diffraction to probe for:
 - Lattice defects (e.g. – oxygen vacancy formation)
 - Non-ambient condition structural changes
- Structural modifications lead to changes in Co oxidation state that affect superconductivity in $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$

Determining the Superconducting Phase Diagram Using a Single Sample



Oxygen vacancy formation changes the cobalt oxidation state in $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ over time. This allows mapping of the SC phase diagram using a single sample!

Thermal Expansion and Compressibility



Application of P induces an increase in the CoO_2 layer thickness. This reduction in Co valence is due to charge redistribution between Co–O and the H-bonds.

